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(21) International Application Number: <b>PCT/EP98/03489</b> (22) International Filing Date: <b>3 June 1998 (03.06.98)</b>  (30) Priority Data: <b>97303924.1</b> <b>6 June 1997 (06.06.97)</b> <b>EP</b> (34) Countries for which the regional or international application was filed: <b>GB et al.</b>  (71) Applicant (for AU BB CA CY GB GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): <b>UNILEVER PLC [GB/GB]; Unilever, Blackfriars, London EC4P 4BQ (GB).</b>  (71) Applicant (for all designated States except AU BB CA CY GB GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW): <b>UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</b>  (72) Inventors: <b>BOSKAMP, Jelles, Vincent, Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Rotterdam (NL). LEMPERS, Edwin, Leo, Mario; Lever Development Centre, Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).</b>		(74) Agent: <b>ELLIOT, Peter, William; Unilever PLC, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).</b>  (81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b>  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: <b>CLEANING COMPOSITIONS IN TABLET FORM</b>			
(57) Abstract  A tablet of compacted particulate cleaning composition which contains surfactant and detergency builder, and is suitable for fabric washing also includes water-insoluble, water-swellable polymeric material, and disintegration-promoting particles containing at least 40 % (by weight of the particles) of one or more materials selected from: compounds with a water-solubility exceeding 50 grams per 100 grams water, phase I sodium tripolyphosphate, sodium tripolyphosphate which is partially hydrated so as to contain water of hydration in an amount which is at least 0.5 % by weight of the sodium tripolyphosphate in the disintegration-promoting particles.			

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## CLEANING COMPOSITIONS IN TABLET FORM

This invention relates to cleaning compositions in the form of tablets for use in fabric washing.

5 Detergent compositions in tablet form are described, for example, in GB 911204 (Unilever), US 3953350 (Kao), JP 60-015500A (Lion) and EP-A-711827 (Unilever); and are sold commercially in Spain. Tablets have advantages over powdered products in that they do not require measuring and  
10 are thus easier to handle and dispense into the washload.

Tablets of a detergent composition are generally made by compressing or compacting a quantity of the composition in particulate form. It is desirable that tablets have adequate strength when dry, yet disperse and dissolve  
15 quickly when added to wash water. In such tablets the surfactant functions as a binder, plasticising the tablet. However, it can also retard disintegration of the tablet by forming a viscous gel when the tablet comes into contact with water.

20 It can be difficult, to obtain both tablet strength and an ability to disperse and dissolve quickly in the wash liquor. Tablets formed using only a light compaction pressure tend to crumble and disintegrate on handling and packing; while more strongly compacted tablets may be

sufficiently cohesive but then fail to disintegrate or disperse to an adequate extent in the wash.

This problem has proved especially acute with tablets formed by compressing powders containing surfactant and  
5 built with insoluble detergency builder such as sodium aluminosilicate (zeolite).

It is known to include materials whose function is to enhance disintegration of tablets when placed in wash water. Some tablets which are sold commercially  
10 incorporate urea for this purpose. Urea has a very high solubility in water exceeding 100gms per 100ml water at 20°C.

We have now found that the disintegration of tablets of cleaning composition can be accelerated by incorporating in  
15 the tablet a quantity of a water-insoluble but water-swallowable polymeric material.

However, we have observed that particles of water-swallowable but water-insoluble material which are effective to cause tablet disintegration are liable to be retained on the  
20 washed laundry as visible residues.

We therefore propose, in the present invention, that the disintegration and dissolution of tablets is brought about by a combination of two materials. One is a water-

swellable but water-insoluble polymeric material. The other is a water-soluble compound which enhances dissolution.

According to the present invention, there is provided a  
5 tablet of compacted particulate cleaning composition,  
containing overall from 5 to 50 wt% surfactant and from 5  
to 80 wt% detergency builder wherein the tablet or a  
discrete region thereof which contains surfactant and  
detergency builder also contains (i) water-insoluble,  
10 water-swellable polymeric material, and (ii) particles  
functioning to aid and dissolution/disintegration and  
containing at least 40% (by weight of these particles (ii))  
of one or more materials selected from

- compounds with a water-solubility exceeding 50 grams  
15 per 100 grams water
- phase I sodium tripolyphosphate or
- sodium tripolyphosphate which is partially hydrated so  
as to contain water of hydration in an amount which is  
at least 0.5% by weight of the sodium tripolyphosphate  
20 in the particles.

As will be explained further below, these disintegration-promoting particles can also contain other forms of tripolyphosphate or other salts within the balance of their composition.

25 A tablet of the invention may be either homogeneous or

heterogeneous. In the present specification, the term "homogeneous" is used to mean a tablet produced by compaction of a single particulate composition, but does not imply that all the particles of that composition will necessarily be of identical composition. The term "heterogeneous" is used to mean a tablet consisting of a plurality of discrete regions, for example layers, inserts or coatings, each derived by compaction from a particulate composition. In a heterogeneous tablet according to the present invention, each discrete region of the tablet will preferably have a mass of at least 5gm.

In a heterogeneous tablet, at least one of the discrete regions contains the said swellable polymeric material and disintegration-promoting particles together with surfactant and detergency builder in accordance with the invention.

A preferred tablet or a discrete region thereof contains from 2 or 5wt% up to 40 or 50wt% surfactant, from 5 or 10 up to 60 or 80wt% detergency builder and from 0.5 to 10wt% of the water-insoluble but swellable polymeric material. Where a tablet is heterogeneous, these percentage ranges for surfactant and builder may apply to the overall composition of the tablet, as well as to at least one discrete region of the tablet.

If the material in the disintegration-promoting particles can function as a detergency builder, (as is the case with

sodium tripolyphosphate) then of course it contributes to the total quantity of detergency builder in the tablet composition.

The quantity of disintegration-promoting particles is suitably from 5 or 8 wt% up to 25 or 40 wt% of the tablet or region thereof. Benefits from water-insoluble, swellable polymeric material can be obtained when it is present in amounts from 0.5 better 0.9 up to at least 2.7 or 3.5 wt% of the tablet or region thereof. It may possibly be used in larger amounts such as up to 5 or 8wt%.

In a heterogenous tablet, the polymeric material may be incorporated in some only of a plurality of discrete regions (eg. in only one of two) while other region(s) contain a lesser concentration, or more, of the polymeric material. Such an arrangement may be used to cause the regions of the tablet to disintegrate and dissolve (in so far as their constituents are soluble) at different rates.

#### The water-swellable polymer

Suitable water-swellable polymeric materials preferably have sufficient water-absorptivity that they can absorb at least four times their own weight of water, ie. a water uptake of at least 4gm per gm.

A number of such materials are known, and are generally based on cellulose which may be chemically modified to

enhance its water uptake capacity. Sometimes such modified celluloses have ionic substituents but for this invention it is preferred that any substituents are nonionic.

Surprisingly, we have found that such a material is more effective if it has a relatively large particle size. We therefore prefer that the polymeric material has a particle dimension of at least 400 better at least 500 micrometres. Such polymeric material with a particle dimension of at least 400 micrometres is preferably an agglomerate of smaller particles whose largest dimension is no greater than 150 or 200 micrometres, better no greater than 50 micrometres. This makes it possible for at least some of the polymer particles to break up during a wash cycle, and not remain as visible residues in fabrics. While this is advantageous, we have observed that since particles nevertheless remain intact and can be observed as residues.

The material may exist as relatively rounded particles, or as relatively flat particles such as flakes or discs. In the latter case a dimension (diameter) of the flakes will be larger, perhaps substantially larger, than the diameter of a sphere with the same volume.

The largest dimension of particles of the polymeric material may be determined by sieve analysis, and the shape of the particles can be observed under a microscope.



It is customary to use sodium carboxymethylcellulose (SCMC) in detergent compositions, usually as not more than 3 wt% of the composition. We have found that such quantities of SCMC are generally ineffective to promote tablet  
5 disintegration.

We have found it desirable to use swellable polymeric materials with little or no ionic character. Such materials may be polysaccharides with little or no ionic substitution.

10 The absence or near absence of ionic substitution can be expressed by stating that the charge density of the polymeric material is low, such as less than  $10^{-3}$ , better less than  $6 \times 10^{-4}$  or even zero. The term "charge density" denotes the number of charges on a polymer molecule divided  
15 by the molecular weight of the polymer. It is essentially the same as the average number of charges on a repeat unit of the polymer divided by the average molecular weight of a repeat unit.

The water-insoluble, water-swellable polymeric material is  
20 preferably added as particles which contain such material as at least 75% of the anhydrous weight of these particles (ie. ignoring their moisture content). Usually they will contain little or nothing except the polymer and any accompanying moisture.

Disintegration-promoting particles

One possibility is that these particles contain at least 40% of their own weight, better at least 50%, of a material which has a solubility in deionised water at 20°C of at least 50 grams per 100 grams of water.

The said particles may provide material of such solubility in an amount which is at least 7 wt% or 12 wt% of the whole composition of the tablet or discrete region thereof.

A solubility of at least 50 grams per 100 grams of water at 20°C is an exceptionally high solubility: many materials which are classified as water soluble are less soluble than this.

Some highly water-soluble materials which may be used are listed below, with their solubilities expressed as grams of solid to form a saturated solution in 100 grams of water at 20°C:-

<u>Material</u>	<u>Water Solubility (g/100g)</u>
Sodium citrate dihydrate	72
Potassium carbonate	112
Urea	>100
Sodium acetate	119
Sodium acetate trihydrate	76
Magnesium sulphate 7H <sub>2</sub> O	71

By contrast the solubilities of some other common materials at 20°C are:-

<u>Material</u>	<u>Water Solubility (g/100g)</u>
Sodium chloride	36
5 Sodium sulphate decahydrate	21.5
Sodium carbonate anhydrous	8.0
Sodium percarbonate anhydrous	12
Sodium perborate anhydrous	3.7
Sodium tripolyphosphate anhydrous	15

10 Preferably this highly water soluble material is incorporated as particles of the material in a substantially pure form (i.e. each such particle contains over 95% by weight of the material). However, the said particles may contain material of such solubility in a  
15 mixture with other material, provided that material of the specified solubility provides at least 40% by weight of these particles.

It may be preferred that the highly water-soluble material is a salt which dissolves in water in an ionised form. As  
20 such a salt dissolves it leads to a transient local increase in ionic strength which can assist disintegration of the tablet by preventing nonionic surfactant from swelling and inhibiting dissolution of other materials.

Another possibility is that the said particles which  
25 promote disintegration are particles containing sodium tripolyphosphate with more than 40% (by weight of the

particles) of the anhydrous phase I form.

Sodium tripolyphosphate is very well known as a sequestering builder in detergent compositions. It exists in a hydrated form and two crystalline anhydrous forms.

5 These are the normal crystalline anhydrous form, known as phase II which is the low temperature form, and phase I which is stable at high temperature. The conversion of phase II to phase I proceeds fairly rapidly on heating above the transition temperature, which is about 420°C, but  
10 the reverse reaction is slow. Consequently phase I sodium tripolyphosphate is metastable at ambient temperature.

A process for the manufacture of particles containing a high proportion of the phase I form of sodium tripolyphosphate by spray drying below 420°C is given in  
15 US-A-4536377.

Particles which contain this phase I form will often contain the phase I form of sodium tripolyphosphate as at least 50% or 55% by weight of the tripolyphosphate in the particles.

20 Suitable material is commercially available. Suppliers include Rhone-Poulenc, France and Albright & Wilson, UK.

Another possibility is that the particles which promote disintegration are particles which contain at least 40 wt%

sodium tripolyphosphate which is partially hydrated. The extent of hydration should be at least 0.5% by weight of the sodium tripolyphosphate in the particles. It may lie in a range from 0.5 to 4%, or it may be higher. Indeed  
5 fully hydrated sodium tripolyphosphate may be used to provide these particles.

It is possible that the particles contain at least 40 wt% sodium tripolyphosphate which has a high phase I content but is also sufficiently hydrated so as to contain at least  
10 0.5% water by weight of the sodium tripolyphosphate.

The remainder of the tablet composition used to form the tablet or region thereof may include additional sodium tripolyphosphate. This may be in any form, including sodium tripolyphosphate with a high content of the  
15 anhydrous phase II form.

When the said particles contain sodium tripolyphosphate, it is preferable that they provide sodium tripolyphosphate, in a quantity which is at least 8%, e.g. 8 to 30%, by weight of the composition of the tablet or region thereof.

20 A zero phosphate tablet in accordance with this invention will utilise disintegration-promoting particles containing material with solubility of at least 50gm/100gm.

Such material may also be used in phosphate built tablets,

but it is more likely that these will utilise particles containing phase I and/or hydrated sodium tripolyphosphate.

When the particles contain sodium tripolyphosphate, it will function as a builder after the tablet or tablet region  
5 disintegrates and dissolves the wash liquor.

The total quantity of sodium tripolyphosphate, in all forms, present in a tablet composition may lie in a range from 15 to 60% by weight of the tablet. Therefore it will be appreciated that the overall quantity of sodium  
10 tripolyphosphate may be provided at least partially by other material in addition to the said particles.

The said particles to promote disintegration will generally be mixed with other particles containing the surfactant, at least some builder and other constituents of the  
15 composition, to provide the overall composition which is compacted into a tablet or a region of a tablet.

#### Surfactant Compounds

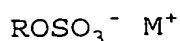
Compositions which are compacted to form tablets or tablet regions of this invention generally contain one or more  
20 organic detergent surfactants. In a fabric washing composition, these preferably provide from 5 to 50% by weight of the overall tablet composition, more preferably from 8 or 9% by weight of the overall composition up to 40% or 50% by weight. Surfactant may be anionic (soap or non-

soap), cationic, zwitterionic, amphoteric, nonionic or a combination of these.

Anionic surfactant may be present in an amount from 0.5 to 50% by weight, preferably from 2% or 4% up to 30% or 40% by weight of the tablet composition.

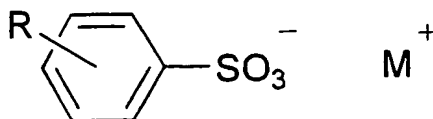
Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of  $C_8-C_{15}$ ; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

Primary alkyl sulphate having the formula



in which R is an alkyl or alkenyl chain of 8 to 18 carbon atoms especially 10 to 14 carbon atoms and  $M^+$  is a solubilising cation, is commercially significant as an anionic surfactant.

Linear alkyl benzene sulphonate of the formula



where R is linear alkyl of 8 to 15 carbon atoms and  $M^+$  is a

solubilising cation, especially sodium, is also a commercially significant anionic surfactant.

Frequently, such linear alkyl benzene sulphonate or primary alkyl sulphate of the formula above, or a mixture thereof  
5 will be the desired anionic surfactant and may provide 75 to 100 wt% of any anionic non-soap surfactant in the composition.

In some forms of this invention the amount of non-soap anionic surfactant lies in a range from 5 to 20 wt% of the  
10 tablet composition.

It may also be desirable to include one or more soaps of fatty acids. These are preferably sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or  
15 hardened rapeseed oil.

Suitable nonionic surfactant compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl  
20 phenols with alkylene oxides, especially ethylene oxide.

Specific nonionic surfactant compounds are alkyl ( $C_{8-22}$ ) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic  $C_{8-20}$  primary or



secondary alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-diamine.

5 Especially preferred are the primary and secondary alcohol ethoxylates, especially the C<sub>9-11</sub> and C<sub>12-15</sub> primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

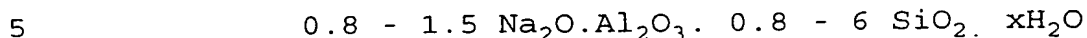
10 In certain forms of this invention the amount of nonionic surfactant lies in a range from 4 to 40%, better 4 or 5 to 30% by weight of the composition. Many nonionic surfactants are liquids. These may be absorbed onto particles of the composition, prior to compaction into tablets.

#### Detergency Builder

15 A composition which is compacted to form tablets or tablet regions will generally contain from 5 better 15 wt% up to 80%, more usually 15 to 60% by weight of detergency builder. This may be provided wholly by water soluble materials, or may be provided in large part or even  
20 entirely by water-insoluble material with water-softening properties. Water-insoluble detergency builder may be present as 5 to 80 wt%, better 5 to 60 wt% of the composition.

Alkali metal aluminosilicates are strongly favoured as

environmentally acceptable water-insoluble builders for fabric washing. Alkali metal (preferably sodium) aluminosilicates may be either crystalline or amorphous or mixtures thereof, having the general formula:



These materials contain some bound water (indicated as  $x\text{H}_2\text{O}$ ) and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5  $\text{SiO}_2$  units (in the formula  
10 above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB  
15 1429143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well known commercially available zeolites A and X, the newer zeolite P described and claimed in EP 384070 (Unilever) and mixtures thereof.

20 Conceivably a water-insoluble detergency builder could be a layered sodium silicate as described in US 4664839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated as "SKS-6"). NaSKS-6 has the delta- $\text{Na}_2\text{SiO}_5$  morphology form of layered

silicate. It can be prepared by methods such as described in DE-A-3,417,649 and DE-A-3,742,043. Other such layered silicates, such as those having the general formula  $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used.

Water-soluble phosphorus-containing inorganic detergency builders, include the alkali-metal orthophosphates, metaphosphates, pyrophosphates and polyphosphates.

Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, orthophosphates and hexametaphosphates. As mentioned above, sodium tripolyphosphate (if any) included in the said particles to promote disintegration will also be part of the detergency builder.

Non-phosphorus water-soluble builders may be organic or inorganic. Inorganic builders that may be present include alkali metal (generally sodium) carbonate; while organic builders include polycarboxylate polymers, such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphonates, monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono- di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates and hydroxyethyliminodiacetates.

Tablet compositions preferably include polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers which can function as builders and also inhibit unwanted deposition onto fabric from the wash liquor.

#### 5    Bleach System

Tableted detergent compositions according to the invention may contain a bleach system. This preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in  
10    conjunction with activators to improve bleaching action at low wash temperatures. If any peroxygen compound is present, the amount is likely to lie in a range from 10 to 25% by weight of the composition.

Preferred inorganic persalts are sodium perborate  
15    monohydrate and tetrahydrate, and sodium percarbonate, advantageously employed together with an activator. Bleach activators, also referred to as bleach precursors, have been widely disclosed in the art. Preferred examples include peracetic acid precursors, for example,  
20    tetraacetylene diamine (TAED), now in widespread commercial use in conjunction with sodium perborate; and perbenzoic acid precursors. The quaternary ammonium and phosphonium bleach activators disclosed in US 4751015 and US 4818426 (Lever Brothers Company) are also of interest.  
25    Another type of bleach activator which may be used, but which is not a bleach precursor, is a transition metal

catalyst as disclosed in EP-A-458397, EP-A-458398 and EP-A-549272. A bleach system may also include a bleach stabiliser (heavy metal sequestrant) such as ethylenediamine tetramethylene phosphonate and  
5 diethylenetriamine pentamethylene phosphonate.

#### Other Detergent Ingredients

The detergent tablets of the invention may also contain one of the detergency enzymes well known in the art for their ability to degrade and aid in the removal of various soils  
10 and stains. Suitable enzymes include the various proteases, cellulases, lipases, amylases, and mixtures thereof, which are designed to remove a variety of soils and stains from fabrics. Examples of suitable proteases are Maxatase (Trade Mark), as supplied by Gist-Brocades  
15 N.V., Delft, Holland, and Alcalase (Trade Mark), and Savinase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark. Detergency enzymes are commonly employed in the form of granules or marumes, optionally with a protective coating, in amount of from about 0.1% to  
20 about 3.0% by weight of the composition; and these granules or marumes present no problems with respect to compaction to form a tablet.

The detergent tablets of the invention may also contain a fluorescer (optical brightener), for example, Tinopal  
25 (Trade Mark) DMS or Tinopal CBS available from Ciba-Geigy AG, Basel, Switzerland. Tinopal DMS is disodium 4,4'-bis-

(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene disulphonate; and Tinopal CBS is disodium 2,2'-bis-(phenylstyryl) disulphonate..

An antifoam material is advantageously included, especially if a detergent tablet is primarily intended for use in front-loading drum-type automatic washing machines.

Suitable antifoam materials are usually in granular form, such as those described in EP 266863A (Unilever). Such antifoam granules typically comprise a mixture of silicone oil, petroleum jelly, hydrophobic silica and alkyl phosphate as antifoam active material, sorbed onto a porous absorbed water-soluble carbonate-based inorganic carrier material. Antifoam granules may be present in an amount up to 5% by weight of the composition.

It may also be desirable that a detergent tablet of the invention includes an amount of an alkali metal silicate, particularly sodium ortho-, meta- or disilicate. The presence of such alkali metal silicates at levels, for example, of 0.1 to 10 wt%, may be advantageous in providing protection against the corrosion of metal parts in washing machines, besides providing some measure of building and giving processing benefits in manufacture of the particulate material which is compacted into tablets. A composition for fabric washing will generally not contain more than 15 wt% silicate. A tablet for machine dishwashing will frequently contain at least 20 wt% silicate.

Further ingredients which can optionally be employed in fabric washing detergent tablet of the invention include anti-redeposition agents such as sodium carboxymethylcellulose, straight-chain polyvinyl pyrrolidone and the cellulose ethers such as methyl cellulose and ethyl hydroxyethyl cellulose, fabric-softening agents; heavy metal sequestrants such as EDTA; perfumes; and colorants or coloured speckles.

#### Particle Size and Distribution

10 A detergent tablet of this invention, or a discrete region of such a tablet, is a matrix of compacted particles.

Preferably the particulate composition has an average particle size in the range from 200 to 2000  $\mu\text{m}$ , more preferably from 250 to 1400  $\mu\text{m}$ . Fine particles, smaller  
15 than 180  $\mu\text{m}$  or 200  $\mu\text{m}$  may be eliminated by sieving before tableting, if desired, although we have observed that this is not always essential.

While the starting particulate composition may in principle have any bulk density, the present invention is especially  
20 relevant to tablets made by compacting powders of relatively high bulk density, because of their greater tendency to exhibit disintegration and dispersion problems. Such tablets have the advantage that, as compared with a tablet derived from a low bulk density powder, a given dose  
25 of composition can be presented as a smaller tablet.

Thus the starting particulate composition may suitably have a bulk density of at least 400 g/litre, preferably at least 500 g/litre, and possibly at least 600 g/litre.

5 A composition which is compacted into a tablet or tablet region may contain particles which have been prepared by spray-drying or granulation and which contain a mixture of ingredients. Such particles may contain the surfactant and some or all of the detergency builder.

10 Granular detergent compositions of high bulk density prepared by granulation and densification in a high-speed mixer/granulator, as described and claimed in EP 340013A (Unilever), EP 352135A (Unilever), and EP 425277A (Unilever), or by the continuous granulation/densification processes described and claimed in EP 367339A (Unilever)  
15 and EP 390251A (Unilever), are inherently suitable for use in the present invention.

Preferably, separate particles of water-insoluble, water-swella-  
ble polymeric material, and the said particles which promote disintegration, are both mixed with the remainder  
20 of the particulate composition prior to compaction.

#### Tableting

Tableting entails compaction of a particulate composition. A variety of tableting machinery is known, and can be used. Generally it will function by stamping a quantity of the



particulate composition which is confined in a die.

Tableting may be carried out at ambient temperature or at a temperature above ambient which may allow adequate strength to be achieved with less applied pressure during  
5 compaction. In order to carry out the tableting at a temperature which is above ambient, the particulate composition is preferably supplied to the tableting machinery at an elevated temperature. This will of course supply heat to the tableting machinery, but the machinery  
10 may be heated in some other way also.

If any heat is supplied, it is envisaged that this will be supplied conventionally, such as by passing the particulate composition through an oven, rather than by any application of microwave energy.

15 The size of a tablet will suitably range from 10 to 160 grams, preferably from 15 to 60 g, depending on the conditions of intended use, and whether it represents a dose for an average load in a fabric washing or dishwashing machine or a fractional part of such a dose. The tablets may  
20 be of any shape. However, for ease of packaging they are preferably blocks of substantially uniform cross-section, such as cylinders or cuboids. The overall density of a tablet preferably lies in a range from 1040 or 1050gm/litre up to 1300gm/litre. The tablet density may well lie in a  
25 range up to no more than 1250 or even 1200gm/litre.

Example 1

Tablets for use in fabric washing were made, starting with a spray-dried base powder of the following composition:

	Ingredient	Parts by Weight
5	Sodium linear alkylbenzene sulphonate	11.0
	Sodium tripolyphosphate*	16.8
	C <sub>13-15</sub> fatty alcohol 7EO	2.4
	C <sub>13-15</sub> fatty alcohol 3EO	2.3
10	Sodium silicate	4.0
	Soap	0.21
	Acrylate/maleate copolymer	1.5
	Sodium sulphate, moisture and minor ingredients	balance to 45 parts

- 15           \*     Added to the slurry as anhydrous sodium tripolyphosphate containing at least 70% phase II form.

A number of particulate compositions were made by mixing this powder with other ingredients as tabulated below. These included particles of sodium tripolyphosphate specified to contain 70% phase I form and contain 3.5% water of hydration (Rhodia-Phos HPA 3.5 available from Rhone-Poulenc).

25     The added ingredients also included particles of water-insoluble water-swellable polymeric material. This material was derived from cellulose and supplied by

Rettenmaier GmbH as "Arbocel A1". It was in the form of particles with a range of shapes and particle sizes (as determined by sieve analysis) with an average diameter of 1mm. It was found to have a water-uptake of 5.7 gm/gm.

- 5 For some compositions this material was sieved to provide a fraction with a narrower range of particle size.

The compositions were balanced to 100% by including varying amounts of dense anhydrous sodium carbonate.

- 10 The various compositions contained the following percentages by weight:

Ingredient	% by weight
Base powder	45.0
Sodium percarbonate granules	15.0
TAED granules	3.4
15 Anti-foam granules	3.2
Perfume, enzymes and other minor ingredients	3.5
HPA tripolyphosphate	variable, 15 to 30%
Water-swellaable polymer	variable, 0 to 5%
20 Sodium carbonate	balance, 0 to 15%

40g portions of each composition were made into cylindrical tablets of 44 mm diameter, using a Fette pilot plant press, so as to produce tablets with density in a range from 1100 to 1250kg/m<sup>3</sup>.

The strength of these tablets was measured using an Instron universal testing machine to compress a tablet until fracture. The value of diametral fracture stress (DFS) was then calculated using the equation

5 
$$\sigma = \frac{2P}{\pi Dt}$$

where  $\sigma$  is the diametral fracture stress in Pascals, P is the applied load in Newtons to cause fracture, D is the tablet diameter in metres and t is the tablet thickness in  
10 metres.

The break-up, dispersion and dissolution of tablets was measured by a test procedure in which a tablet is placed on a plastic sieve with 2mm mesh size which was immersed in 9 litres of demineralised water at ambient temperature of  
15 22°C and rotated at 200 rpm. The water conductivity was monitored until it reached a constant value.

The time for break up and dispersion of the tablets was taken as the time ( $T_{90}$ ) for change in the water conductivity to reach 90% of its final magnitude. This was also  
20 confirmed by visual observation of the material remaining on the rotating sieve. Additionally, the initial gradient of a graph of conductivity against time was noted and expressed as a normalised value relative to that of one of the compositions.

The percentages of HPA tripolyphosphate, and polymeric material, together with the DFS and conductivity results are set out in the following table:

#	HPA tripolyphosphate	polymeric material	balancing carbonate	DFS (kPa)	T <sub>90</sub> (minute)	Gradient of conductivity /time curve
5 1A	30%	0	0	43	3.0	1
1B	27.5%	0	2.5%	30	2.5	2
1C	15%	0	15%	32	8.7	1
1D	24%	2% as supplied	4%	32	3.2	3.3
1E	15%	5% as supplied	10%	18	1.6	26
10 1F	20%	1.5% as supplied	8.5%	50	6.0	2.3
1G	15%	5% 470-800 $\mu$	10%	30	3.2	16
1H	15%	5% 800-1400 $\mu$	10%	21	1.4	23
1J	15%	3% 800-1400 $\mu$	12%	33	2.8	16

Example 2

Tablets with a weight of 40g were prepared as in Example 1, using the same spray dried base powder, but different added ingredients, as set out in the following table:

5	Ingredient	% by weight
	Base powder	58.0
	Polyvinylpyrrolidone	0.6
	Anti-foam granules	4.2
	Perfume, enzymes and other minor ingredients	2.0
10	Sodium citrate dihydrate	20.0
	Water-swellable polymer 800-1400 $\mu$	3.0
	Sodium carbonate	balance to 100%

Example 3

Tablets for use in fabric washing were made, starting with  
 15 a base powder of the following composition:

	Ingredient	parts by weight
	Sodium linear alkylbenzene sulphonate	10.7
	C <sub>13-15</sub> fatty alcohol 7EO.	1.7
	C <sub>13-15</sub> fatty alcohol 3EO.	3.1
20	Zeolite A24	21.0
	Sodium carbonate	3.7
	Sodium citrate dihydrate	3.1
	moisture and minors	5.6
	TOTAL	48.9

Three particulate compositions were made by mixing this powder with other ingredients as set out in the table below. The water-swellaable polymer was "Arbocel A1" used as supplied. Portions of each composition, with a weight of 40g, were compacted into tablets using compaction pressures such that the tablets had equal values of Diametral Fracture Strength, measured as in Example 1 above. They were tested for disintegration and dissolution as in Example 1 and the T<sub>90</sub> conductivity values are shown at the foot of the table.

Ingredient	% by weight		
Base powder	48.9	48.9	48.9
Sodium perborate monohydrate	13.9	13.9	13.9
TAED granules	5.3	5.3	5.3
Anti-foam granules	2.0	2.0	2.0
Fluorescer granules	1.2	1.2	1.2
Sodium silicate granules	3.7	3.7	3.7
Acrylate/maleate copolymer	1.0	1.0	1.0
Perfume, enzymes and other minor ingredients	3.5	3.5	3.5
Sodium acetate trihydrate	18	14.5	11.0
Water-swellaable polymer	0	1.0	2.0
Sodium carbonate	2.5	5.0	7.5
TOTAL	100	100	100
T <sub>90</sub> (minutes)	>10	8.3	5.7

Example 4

The procedure of the previous example was repeated, using a base powder containing primary alkyl sulphate in place of alkyl benzene sulphate as the anionic surfactant. One composition contained 3wt% of "Arbocel A1". It was observed to have a  $T_{90}$  time of 2 minutes. A comparative composition without "Arbocel A1", made with the same DFS value of 33kPa, had a  $T_{90}$  time of 7.5 minutes.

Example 5

Tablets with a weight of 40g for use in fabric washing were made, starting with a granulated base powder of the following composition:

Ingredient	parts by weight
Sodium linear alkylbenzene sulphonate	7.7
C <sub>13-15</sub> fatty alcohol 7EO.	3.5
C <sub>13-15</sub> fatty alcohol 3EO.	3.7
Zeolite A24	25.2
Sodium citrate dihydrate	2.6
Sodium sulphate, moisture and minors	balance to 50 parts



This powder was then mixed with further ingredients to form particulate compositions which were then compacted into tablets as in previous examples. These compositions were as follows:

5	Ingredient	% by weight	
	Base powder	50.0	67.0
	Sodium perborate monohydrate	14.3	-
	TAED granules	5.5	-
	Anti-foam granules	1.0	2.0
10	Fluorescer granules	1.0	-
	Sodium silicate granules	3.7	-
	Acrylate/maleate copolymer	1.0	1.8
	Sodium carbonate	-	3.2
	Water-swellaable polymer	3.0	3.0
15	Sodium citrate dihydrate	18	20
	Perfume, enzymes and other minor ingredients	2.5	3.0

CLAIMS:

1. A tablet of compacted particulate composition,  
containing overall from 5 to 50 % by weight of surfactant and  
from 5 to 80% by weight of detergency builder wherein the  
5 tablet or a discrete region thereof which contains surfactant  
and detergency builder also includes water-insoluble, water-  
swellable polymeric material, and disintegration-promoting  
particles containing at least 40% (by weight of the  
particles) of one or more materials selected from the group  
10 consisting of

- compounds with a water-solubility exceeding 50 grams per  
100 grams water
- phase 1 sodium tripolyphosphate
- sodium tripolyphosphate which is partially hydrated so  
15 as to contain water of hydration in an amount which is  
at least 0.5% by weight of the sodium tripolyphosphate  
in the particles.

2. A tablet according to claim 1 wherein the  
disintegration-promoting particles contain at least 40% (by  
20 weight of the particles) of one or more compounds selected  
from urea, salts with a water-solubility exceeding 50gm.per  
100gms water, and mixtures thereof.

3. A tablet according to claim 1 wherein said  
disintegration-promoting particles in the tablet or region  
25 thereof contain at least 40% (by weight of the particles) of

phase I sodium tripolyphosphate which is partially hydrated so as to contain water of hydration in a range from 0.5 to 4% by weight of these particles.

4. A tablet according to any one of claims 1 to 3, wherein  
5 the polymeric material has a particle dimension of at least 400 micrometres.

5. A tablet according to any one of claims 1 to 3, wherein the polymeric material has a particle dimension of at least 500 micrometres.

10 6. A tablet according to any one of claims 1 to 5, wherein the polymeric material is substantially nonionic such that the charge density of the polymeric material does not exceed  $10^{-3}$ .

15 7. A tablet according to any one of claims 1 to 6, wherein the polymeric material is a polysaccharide.

8. A tablet according to any one of claims 1 to 7, wherein the tablet or discrete region thereof contains 0.1 to 8 wt% of said particles containing water-insoluble, water-swella-  
20 ble polymeric material, and from 5 to 40 wt% of said further particles to promote disintegration.

9. A tablet according to any one of claims 1 to 8, wherein the tablet or said discrete region thereof contains from 0.5

to 3.5 wt% of the polymeric material.

10. A tablet according to claim 8 or claim 9, wherein the tablet or said discrete region thereof contains from 8 to 25 wt% of said further particles to promote disintegration.

5 11. A tablet according to any one of claims 1 to 10, wherein the said detergency builder in the tablet or region thereof comprises water-insoluble detergency builder in an amount from 5 to 60% by weight of the tablet or said region thereof.

10 12. A tablet according to any one of claims 1 to 11, which tablet contains a plurality of discrete regions at least one of which contains a quantity of the said polymeric material while at least one other region of the tablet contains a lesser concentration of the polymeric material or none at all.

15 13. A tablet according to any one of claims 1 to 11 which has at least two layers, the composition in at least one layer containing surfactant, detergency builder and the polymeric material, while at least one other layer contains a lesser concentration of the polymeric material or none at  
20 all.

14. A tablet according to any one of claims 1 to 13 which overall contains 5 to 60 wt% water-insoluble detergency builder.

15. A tablet according to any one of claims 1 to 13 which overall contains from 10 to 80% by weight of water-soluble detergency builder.

16. A tablet according to any one of claims 1 to 15 which  
5 overall contains 8 to 49% by weight of surfactant.

17. Process for making a detergent tablet as claimed in any one of the preceding claims 1 to 16, which comprises mixing water-insoluble, water-swellaable polymeric material, and particles containing at least 40% (by weight of the  
10 particles) of one or more materials selected from the group consisting of

- compounds with a water-solubility exceeding 50 grams per 100 grams water,
- phase 1 sodium tripolyphosphate, and
- 15 • sodium tripolyphosphate which is partially hydrated so as to contain water of hydration in an amount which is at least 0.5% by weight of the sodium tripolyphosphate in the particles

with other particulate ingredients so as to form a  
20 particulate detergent composition which includes surfactant and detergency builder and compacting a quantity of the particulate composition in a mould so that it forms a tablet or a region of a tablet.

18. Process according to claim 17 wherein the swellaable  
25 polymeric material is added to the other particulate

ingredients as particles which contain at least 75% of their own weight of the polymeric material.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/03489

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C11D17/00 C11D3/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
P, X	EP 0 839 906 A (UNILEVER PLC ET AL) 6 May 1998  see the whole document ---	1,3, 7-10, 15-17
X	EP 0 716 144 A (UNILEVER PLC ET AL) 12 June 1996  see examples 2,3 ---	1,2, 7-11,14, 16,17
X	US 3 370 015 A (D. M. VAN KAMPEN ET AL) 20 February 1968 see column 1, line 41 - column 3, line 9; examples 1-6 ---  -/--	1,7-10, 15-18

☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	CH 471 891 A (UNILEVER N. V.) 30 April 1969  see examples 1-3 ----	1,3, 7-10,16, 17
X	EP 0 002 293 A (THE PROCTER & GAMBLE COMPANY ) 13 June 1979 see page 4, line 15 - page 6, line 24; example 4 ----	1,7-10, 15-17
X	WO 95 04804 A (LA MARINA PATENT HOLDING S. A.) 16 February 1995  see page 8, line 3 - page 8, line 23; example 1 -----	1,2, 7-11, 14-17



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/03489

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 839906	A	06-05-1998	GB 2318800 A	06-05-1998
EP 716144	A	12-06-1996	NONE	
US 3370015	A	20-02-1968	NONE	
CH 471891	A	30-04-1969	BE 657846 A	30-06-1965
			DE 1296297 B	
			DK 116612 B	26-01-1970
			FR 1420795 A	02-03-1966
			GB 1093420 A	
			SE 306982 B	16-12-1968
			US 3417024 A	17-12-1968
EP 2293	A	13-06-1979	BE 56 T	18-04-1980
			DE 2857472 A	17-07-1980
			NL 7815064 A	30-05-1980
			NL 7815064 T	30-05-1980
			CA 1109752 A	29-09-1981
			FR 2443502 A	04-07-1980
			GB 2041966 A	17-09-1980
			US 4219435 A	26-08-1980
WO 9504804	A	16-02-1995	CH 686002 A	30-11-1995
			AU 7262294 A	28-02-1995
			CA 2145096 A	16-02-1995
			EP 0663944 A	26-07-1995

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